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Thickness-Dependent Swelling Behavior of Vapor-Deposited Smart Polymer Thin Films

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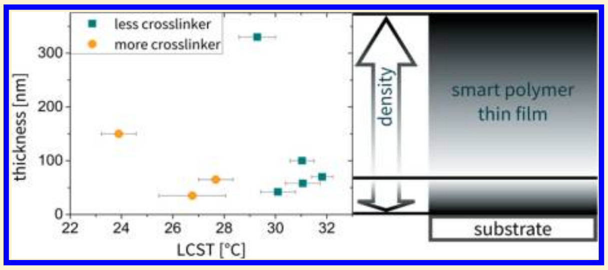
Supporting Information



ABSTRACT: In this contribution, the temperature-dependent swelling behavior of vapor-deposited smart polymer thin films is shown to depend on cross-linking and deposited film thickness. Smart polymers find application in sensor and actuator setups and are mostly fabricated on delicate substrates with complex nanostructures that need to be conformally coated. As initiated chemical vapor deposition (iCVD) meets these specific requirements, the present work concentrates on temperature-dependent swelling behavior of iCVD poly(*N*-isopropylacrylamide) thin films. The transition between swollen and shrunken state and the corresponding lower critical solution temperature (LCST) was investigated by spectroscopic ellipsometry in water. The films' density in the dry state evaluated from X-ray reflectivity could be successfully correlated to the position of the LCST in water and was found to vary between 1.1 and 1.3 g/cm^3 in the thickness range 30−330 nm. This work emphasizes the importance of insights in both the deposition process and mechanisms during swelling of smart polymeric structures.

INTRODUCTION

Hydrogels are networks of hydrophilic polymer chains. In a water environment, either in humidity or in liquid state, water molecules form hydrogen bonds with the hydrophilic groups in the polymeric structure, making the material rearrange and swell up to a multiple of its dry size. Upon changing the amount of water in contact with the polymeric network, the hydrogel reacts reversibly by taking up water into or repelling out water from its inherent structure. This reversible swelling behavior makes this class of materials interesting for a variety of different setups (e.g., in drug delivery,[1] contact lenses).

The kinetics of the water uptake are time-limited by water diffusivity.[2] Therefore, adopting thin polymeric films is crucial for achieving fast response times and, in turn, optimal device performance. However, often the water uptake processes and the corresponding rearrangement of polymer chains impose stress on the thin film and could result in poor adhesion or mechanical failure. Consequently, to ensure mechanical stability during swelling, a specific cross-linking co-monomer can be added. Cross-linking is achieved by adding a chemical species that allows for the binding of two separate polymer chains. This cross-linked hydrogel can, therefore, be seen as a polymer mesh, able to take up a specific amount of water into its structure.[3]

Monomer and cross-linker choice influence the responsiveness to water and to other external stimuli. Specific chemical functionalities in the monomer units can be utilized to fabricate stimuli-responsive hydrogels. A variety of such smart polymers have been demonstrated to respond to temperature, pH, magnetic/electric fields, or different concentrations of specific chemical species (e.g., glucose).[4] In the current study, the most prominent temperature-responsive hydrogel, poly-*N*-isopropylacrylamide (pNIPAAm), has been investigated. Its temperature-responsiveness stems from the molecule exhibiting hydrophilic groups (i.e., amide), forming hydrogen bonds in the presence of water, and the probability for attractive intrachain interactions leading to polymer collapse, depending on the material's temperature.[5] The presence of both functionalities results in interesting thermoresponsive properties, namely, the lower critical solution temperature (LCST). At this temperature, pNIPAAm undergoes a phase transition from a hydrated swollen state to a dehydrated shrunken state, below and above the LCST, respectively. This reversible temperature-dependent swelling behavior attracts particular interest for using smart polymer thin films in sensor[6] and actuator setups.[7]

As in several applications delicate surfaces (e.g., drugs, flexible substrates) need to be coated, often with specific nanostructure, vapor-based techniques are more suitable for the purpose than solution processing due to the absence of solvent-related inconveniences: dissolution of the substrate, intermixing of components, surface tension. In this contribution, initiated chemical vapor deposition (iCVD) was adopted. In this solvent-free technique, monomer, cross-linker, and radical initiator molecules are flown into a vacuum chamber in the gas phase at set flow rates. The initiator (usually a peroxide) decomposes into radicals at a heated filament (200−350 °C) mounted above the sample stage. The monomer and

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cross-linker molecules adsorb on the low temperature substrate (held at 10−40 °C). The initiator radicals attack the unsaturated bonds in the monomer and cross-linker species and, hence, initiate polymerization on the substrate similar to free radical polymerization processes.[8] However, the mild processing conditions allow for full retention of delicate functionalities upon deposition such as thermoresponsive groups, enabling precise engineering of the material properties. With iCVD, accurate control on the film thickness can be achieved via deposition time and accurate tuning of the chemical composition can be achieved by setting the monomer/cross-linker/initiator ratio and by choosing their distinct chemical nature.

The cross-linker content is known to affect the mesh size and, therefore, the degree of swelling of a polymer.[3] Surface attached networks[9] and, in particular, thin films deposited by iCVD[10] have been shown to behave correspondingly. Furthermore, it has been previously reported that cross-linking and its amount within the polymeric structure affect the position of the LCST transition, with the hydrophobicity[11] or hydrophilicity[12] of the cross-linker determining the direction of the shift. However, next to the chemical composition affecting the thermoresponsive properties of the polymer, thickness should also be a crucial parameter affecting the LCST position. In the literature, the LCST of solution-processed photo-cross-linked pNIPAAm-based thin films has been reported to change as a function of film thickness ranging from 20 nm up to 2 μm, with the amount of cross-linking defining the magnitude of this effect.[13] For pNIPAAm thin films with a low amount of cross-linking and film thicknesses up to 100 nm, stable values for the LCST have been reported. Above 100 nm, the films' transition temperature was shown to decrease linearly with increasing film thickness. The state in which the thin films are cross-linked (dry or partially swollen) has been deemed responsible for changes in shape and position of the LCST transition. Swelling is one-dimensional in thin films and introduces compression in the polymeric system in pNIPAAm films cross-linked in the dry state. As the magnitude of this compression changes with film thickness, this results in a thickness-dependent LCST.[13]

As this thickness-dependent swelling behavior is not very well documented for solution-processed polymers and not reported for vapor-deposited thin polymeric films, in this study, we aim at demonstrating the effect of cross-linking and film thickness on the thermoresponsive behavior also for pNIPAAm thin films deposited by initiated chemical vapor deposition. The film thickness range between 30 and 330 nm, most suitable for vapor-based techniques, is investigated, focusing on the low film thickness regime. Results on the applicability of the investigated polymeric system to humidity sensing have previously been reported by our group in Salzmann et al.[14] There, the temperature-dependent swelling behavior of two different polymeric systems in a humid environment has been analyzed and compared. In the present contribution, the iCVD synthesis of one of these systems, namely, p(NIPAAm-*co*-DEGDVE), as already reported by Alf et al.,[15] was used as a case study. Herein, the focus is on fundamental investigations of thin film properties and their connection to thickness-dependent swelling behavior of vapor-deposited systems in water. For this purpose, in the present work, the LCST together with optical properties of the thin films are determined by swelling experiments in water recorded *in situ* by spectroscopic ellipsometry (SE). X-ray reflectivity (XRR) measurements and SE measurements in a controlled environment (nitrogen/humidity) have been carried out, deepening the understanding of the investigated effects in terms of thin film properties.

■ EXPERIMENTAL SECTION

Hydrogel layers of thicknesses ranging between 30 and 330 nm have been deposited in a custom-built initiated chemical vapor deposition (iCVD) reactor. The deposition processes were run in a cylindrical chamber (diameter 360 mm, height 55 mm), in which the pressure during deposition is controlled by a Duo 5M rotary vane pump (Pfeiffer Vacuum, Germany) and a throttle valve (MKS Instruments, USA). Single-sided polished silicon wafers with a native oxide of 1.5−2 nm thickness on top (Siegert Wafer, Germany) are used as substrates. The substrates are positioned on the bottom of the reaction chamber, where the temperature is set to 35 °C by an Accel 500 LC heater/chiller (Thermo Fisher Scientific, USA). The deposited film thickness is monitored *in situ* by laser interferometry with a He−Ne laser (λ = 633 nm; Thorlabs, USA) through a removable quartz glass lid. Di-*tert*-butyl peroxide (TBPO, 98%; Aldrich, Germany) is used as an initiator. TBPO is kept at room temperature in a glass jar connected to the reaction chamber via a needle valve (Swagelok, USA) to be able to set the desired flow rate of 1 sccm. Twenty-five mm above the substrates, a Ni−Cr wire wound in 12 parallel lines (20 mm wire separation) functions as a heated filament (200 °C) to cleave the initiator molecules entering the reaction chamber. *N*-isopropylacrylamide (NIPAAm, 99%; Aldrich, Germany) is used as monomer and di(ethylene glycol) divinyl ether (DEGDVE, 99%; Aldrich, Germany) as cross-linker. NIPAAm and DEGDVE are also kept in glass jars but heated to 85 and 70 °C, respectively. The monomer and cross-linker vapors are flown into the reaction chamber through a heated mixing line (90 °C). Needle valves (Swagelok, USA) are used to set flow rates and achieve controlled composition. Since the deposition rate depends on the individual flow rates, substrate temperature, and working pressure, the film thickness increase as monitored *in situ* by laser interferometry was used to stop the deposition at different deposition times when the desired thickness was achieved.

Spectroscopic ellipsometry (SE) in a wavelength range of 370−1000 nm (M-2000S, J.A. Woollam, USA) was used to determine the film thickness and optical properties of the thin films in a controlled environment (nitrogen, relative humidity, and water at set temperature). A temperature controlled liquid stage (J. A. Woollam, USA) was used for performing swelling experiments in deionized water. The recorded data were evaluated with an optical model consisting of a c-Si semi-infinite layer on the bottom (temperature-dependent), a 1.6 nm thick native SiO_2 layer in the middle, and the polymer film on top. The polymer layer was modeled with a Cauchy function, and an Urbach tail was adopted accounting for adsorption in the low wavelength region. The surrounding medium was set to H_2O with temperature-dependent optical properties. For the temperature-dependent swelling experiments, the liquid stage and the mounted sample (already exposed to deionized water) were precooled to 10 °C. The respective signal was then recorded while applying a temperature ramp from 10 to 50 °C at a heating rate of 0.5 °C/min. Directly after deposition, the thin film samples were rinsed for 30 s with deionized water for equilibration. Despite rinsing, the first and second heating experiments showed differences in shape and position of the transition. As equilibration has been earlier reported to be needed for the study of temperature-dependent behavior of iCVD thin films,[16] the third heating experiment was used for the determination of the LCST, as all of the further heating ramps give similar results. This effect was attributed to the removal of loosely attached material and the rearrangement of polymer chains in the first couple of heating cycles for which rinsing is not sufficient while heavier rearrangements during cooling/heating are (especially in films exhibiting a low amount of cross-linking). As described in detail later, the film thickness changes after rinsing, but together with the optical properties as recorded by SE, it has not been observed to change after

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the first two heating cycles applied for equilibration purposes. This hints to structural rearrangements occurring during equilibration that do not affect the amount of material present on the substrate. The ellipsometry measurements in relative humidity and N_2 atmosphere were performed in a THMS600 temperature stage (Linkam, UK) at room temperature (~25 °C), with the gases being supplied from a custom-built mixing setup. An SHT15 humidity sensor (Sensirion, Switzerland) was used to monitor the relative humidity (RH) in the sample stage *in situ*; the samples were measured after equilibration in the respective environment, so that the film thickness would not change more than 0.5 nm in 5 min. The recorded optical data have been evaluated using the same model as that in the liquid case but with the ambient material being set to air ($n \approx 1$). Likewise, measurements to obtain information about the available free volume detectable with water have been carried out similar to Perrotta et al.[17,18] Therefore, the thin film samples have been kept under a nitrogen atmosphere at a constant temperature (25 °C), determining their optical properties. Subsequently, water vapor has been introduced into the system in 10% RH steps, to which the films respond by filling free volume with H_2O. Hence, the refractive index first increases due to water permeation, which can be understood as a measure for free volume of the respective thin film.

X-ray reflectivity (XRR) measurements were performed on a PANalytical Empyrean diffractometer. The diffractometer uses a copper sealed tube, a multilayer mirror for monochromatizing the beam (λ = 0.154 nm), a beam mask of 10 mm, and a 1/32° divergence slit on the incident beam side. On the diffracted beam side, a receiving slit of 0.1 mm and a 0.02 rad Soller slit were used in front of a PANalytical PIXcel 3D detector in point detector mode. The critical angle of total reflection was read out of the XRR patterns as the angle 2θ slightly above the maximum intensity where the intensity drops to half its maximum value.[19] All of the XRR measurements have been performed at room temperature (~25 °C) and at a relative humidity of ~40%.

Absorbance spectra of several samples were collected in transmission mode on a Bruker IFS 66 v/s Fourier transform infrared (FTIR) spectrometer. The measurements were run in the wavenumber range 1000−4000 cm^{-1} at a resolution of 4 cm^{-1} and a zero filling factor of 8.

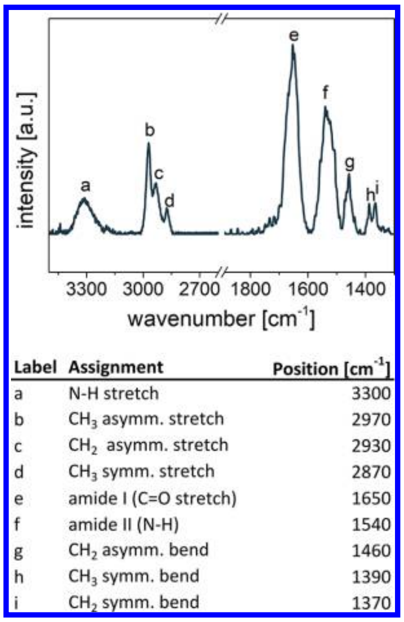
■ RESULTS AND DISCUSSION

A series of thin films of p(NIPAAm-*co*-DEGDVE) with varying amounts of cross-linking and film thickness have been successfully deposited by iCVD, as also previously reported.[14] The respective degree of cross-linking has been set by adjusting the ratio of the monomer, cross-linker, and initiator flow rates. From the flow rates, the nominal composition of the deposited thin films was calculated via the partial pressure of the chemicals compared to their saturation pressure (P_M/P_{sat}) in the applied temperature and pressure conditions. All of the flow rates have been chosen so that the P_M/P_{sat} values lie in the range 0.05−0.2, a regime where surface concentration is reported to depend linearly on the P_M/P_{sat} value.[20] Hence, the presented values of the nominal cross-linker amount correspond to the calculated amount of cross-linker species available on the surface during deposition and, therefore, are related to but do not represent the exact fraction of cross-linker molecules in the respective deposited polymeric system. The following formula has been used to calculate the nominal DEGDVE cross-linker amount from the P_M/P_{sat} values of the components of the deposited polymeric structure (NIPAAm and DEGDVE):

$$\text{crosslinker amount [\%]} = \frac{(P_M/P_{sat})_{DEGDVE}}{(P_M/P_{sat})_{NIPAAm} + (P_M/P_{sat})_{DEGDVE}} \times 100$$

For this investigation, two differently cross-linked polymers of p(NIPAAm-*co*-DEGDVE) were chosen as case models to investigate the effect of cross-linker concentration and overall thin film thickness on the LCST. For the less cross-linked series, the nominal percentage of cross-linking was set to 25%, whereas it was set to 40% for the more cross-linked samples. Additionally, a series of p(NIPAAm-*co*-DEGDVE) samples with a deposited film thickness of 70 nm has been prepared with cross-linker amounts varying between 25 and ~60%.

FTIR absorbance spectra were collected on the differently cross-linked samples with varying film thickness. The presence of the cross-linker could not be determined from FTIR due to DEGDVE lacking strong characteristic FTIR absorption bands, as reported earlier.[15] However, a representative spectrum is shown in Figure 1 to illustrate successful polymerization with the absence of characteristic vinyl group vibrations at 3150, 1620, and 1400 cm^{-1} as labeled by Salzmann et al.[14] The recorded absorption bands compare well to FTIR data of p(NIPAAm-*co*-DEGDVE) films deposited by iCVD in the literature,[15] and all recorded peaks could be successfully assigned to absorption bands within the chemical structure of pNIPAAm according to Sun et al.[21]



Label	Assignment	Position [cm^{-1}]
a	N-H stretch	3300
b	CH_3 asymm. stretch	2970
c	CH_2 asymm. stretch	2930
d	CH_3 symm. stretch	2870
e	amide I (C=O stretch)	1650
f	amide II (N-H)	1540
g	CH_2 asymm. bend	1460
h	CH_3 symm. bend	1390
i	CH_2 symm. bend	1370

Figure 1. FTIR absorption spectrum of a 330 nm 25% cross-linked p(NIPAAm-*co*-DEGDVE) sample indicating successful polymerization by not exhibiting vinyl group absorption bands[14] at 3150, 1620, and 1400 cm^{-1}; peaks labeled and assigned according to Sun et al.[21]

As pure pNIPAAm films dissolve in water, the presence of the cross-linker has been successfully verified by the films' stability upon rinsing, down to a nominal DEGDVE content of 25%. As stated earlier, rinsing leads to the removal of loosely attached material. The amount of material removed decreases with increasing amount of cross-linking, from 7−8% of the deposited dry film thickness for 25%-cross-linked samples to 3−4% for samples with 40% DEGDVE cross-linker fraction, as evaluated from SE measurements. However, the investigated samples within a similarly cross-linked thickness series show similar percentages of material removal during rinsing. This points out that rinsing affects the entire thin film independently of the overall film thickness, instead of just removing material, e.g., from the surface of the sample. Furthermore, proving the presence of the cross-linker at different degrees, the films are able to take up significant amounts of water, in a range going from ~10% (with a high amount of cross-linker) up to 120% of their dry film thickness (with a low amount of cross-linker) at 20 °C (see Figure 2).

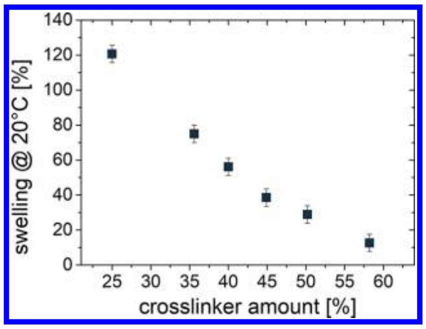


Figure 2. Swelling at 20 °C (thickness in water compared to the dry thickness) as a function of the nominal cross-linker amount (DEGDVE fraction) of differently cross-linked 70 nm-thick p(NIPAAm-*co*-DEGDVE) samples

The LCST values of the respective thermoresponsive thin film samples have been evaluated as the mean values of the points of inflection of thickness and refractive index (measured at 633 nm) curves derived from spectroscopic ellipsometry. The data were acquired in water as a function of temperature during heating from ~15 to 50 °C (see Figure 3 for representative measurement data). The thickness is reported here normalized to the thickness measured at 50 °C, for clarity.

As the film thickness also affects the kinetics of the swelling/deswelling process,[2] several different heating rates between 0.25 and 4 °C/min have been adopted (see the Supporting Information). As a result, a heating rate of 0.5 °C/min has been used for all of the swelling experiments, because kinetic effects can be neglected: Heating ramps at this rate yield similar results as applying lower heating rates for the investigated film thickness regime, while still being sufficiently quick to achieve reasonably constant heating ramps in a room temperature environment.

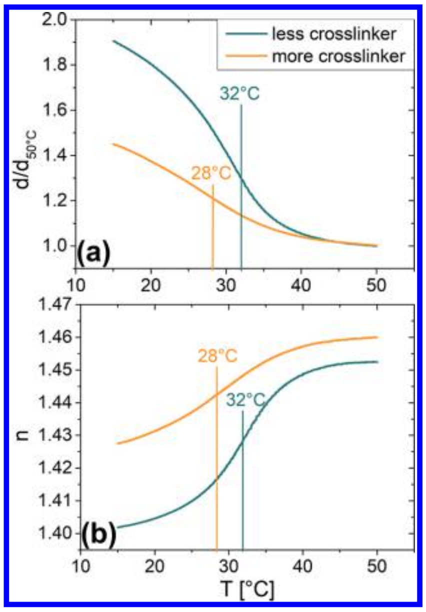


Figure 3. (a) Thickness normalized to the value measured at 50 °C ($d/d_{50°C}$) and (b) refractive index n measured at 633 nm as a function of temperature during heating in water for the evaluation of the LCST as the mean value of the points of inflection of the respective curves plotted for two differently cross-linked 70 nm-thick samples.

As aforementioned and evident from the plots in Figure 3, the cross-linking amount also affects the LCST transition.[12] Two effects have been deemed responsible: First, the mesh size is being reduced by introducing more cross-linker into the polymeric system. Therefore, the maximum amount of water the polymer thin film is able to take up is reduced by increasing the amount of cross-linker.[3] In the investigated systems, the maximum swelling at 20 °C for several differently cross-linked p(NIPAAm-*co*-DEGDVE) thin films (see Figure 2) shows a clearly decreasing trend from 120% for a cross-linking degree of 25% to swelling of approximately 10% for a cross-linking degree of ~60%. Second, the hydrophobic cross-linker DEGDVE makes it favorable for the thin film to repel out water, even at lower temperatures. This leads to a decreased LCST for more cross-linked thin films, whereas the LCST values of the pNIPAAm thin films with a low amount of cross-linking are comparable to pure bulk pNIPAAm hydrogels[22] or solution-processed pNIPAAm layers grafted onto surfaces,[23] exhibiting values of around 32 °C. The LCST values of the photo-cross-linked pNIPAAm thin films reported by Harmon et al.[13] also compare well to the values reported in this study. Also, the magnitude of LCST shifts due to the different amounts of cross-linking are comparable to literature values, as the LCST was reported to shift for ~5 °C when changing the amount of cross-linking from 10 to 30% in p(NIPAAm-*co*-EGDA) films deposited by iCVD.[12] In order to verify the effect of different thin film thickness values on the LCST, heating ramps upon water exposure were measured to obtain the LCST values for p(NIPAAm-*co*-DEGDVE) layers ranging from 30 to 330 nm. The LCST values for two thickness series with different amounts of cross-linking are reported in Figure 4.

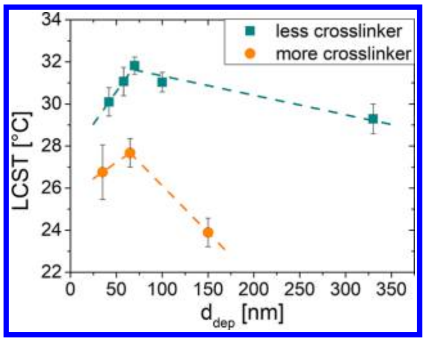


Figure 4. LCST as a function of deposited film thickness (d_{dep}) for differently cross-linked p(NIPAAm-*co*-DEGDVE) thin films (dotted lines are for guidance of the eye).

Both series exhibit a maximum LCST value for a deposited film thickness of ~70 nm, at 27.7 and 31.8 °C for the more and less cross-linked polymers, respectively. Furthermore, the LCST decreases at higher film thickness, with the effect being more pronounced for the less cross-linked films. This is in agreement with what has been found for photo-cross-linked pNIPAAm films by Harmon et al.[13] and, as previously mentioned, explained by film thickness affecting the state of the polymer during swelling compared to the reference state as cross-linked (compression or elongation). The investigated iCVD thin films are deposited at a pressure of 250 mTorr and at a substrate temperature of 35 °C (dry and above the LCST), where Harmon et al. state that a gel that is cross-linked in dry state is always under compression upon swelling, with the compression being greater further from the substrate.[13] Therefore, two regimes have been identified, above and below a certain critical film thickness depending on the amount of cross-linking. Above the critical thickness, the LCST decreases linearly with film thickness. Harmon et al.[13] also report on the LCST being constant below this critical film thickness. However, in the present study, the LCST was found to decrease toward lower film thickness for both series of different amounts of cross-linking, which has not been reported before. Therefore, the present investigations show that the p(NIPAAm-*co*-DEGDVE) thin films deposited by iCVD exhibit a thickness- and cross-linker-dependent swelling behavior, possibly caused by thickness-dependent physical properties of the investigated polymeric systems, as described later.

In order to verify the expected relation between the variation in LCST values and the physical properties of the thin films, the refractive index (n) was recorded in different environments. Refractive index values are a measure for the optical density of thin film samples. Therefore, the index as measured in a nitrogen environment (dry) gives information about the density of the polymeric matrix without the presence of water. These values of n measured at ~25 °C as a function of the film thickness and composition are reported in Figure 5a. The trends for the individual thickness series show similarities to the LCST behavior as a function of deposited film thickness. Temperature-dependent measurements in a nitrogen atmosphere revealed that the polymer layers do not exhibit an LCST transition without the presence of water. Temperature only plays a minor role in a pure nitrogen environment, where the samples show thermal expansion of 0.6% of their film thickness between 20 and 50 °C, independent of the cross-linker amount and the deposited thickness. However, the refractive index values of the polymer layers in water at 50 °C give a measure for water being trapped in the system in the collapsed state (see Figure 5b). Additionally, also the respective thickness values measured in water at 50 °C give evidence that water is retained in the system (in the collapsed state). The percentage of thickness difference compared to the dry state is at around +20% for all samples of both cross-linker series. At high deposited film thickness, the values of n at around 1.46 independent of the cross-linker amount are in agreement with what has been previously reported for this regime.[13] At low film thickness, the refractive index at 50 °C is found to decrease, with the effect being more pronounced for the less cross-linked films. Presumably, higher hydrophobicity (water contact angle of 60−90°)[15] compared to the substrate (water contact angle of ~40°) induces differences in swelling behavior during diffusion for different distances from the substrate and hence film thickness regimes. During swelling, this would lead to a water-rich layer close to the substrate. However, this has not been confirmed from fitting the SE data. With the film thickness being large enough (at around 100 nm), these substrate-induced effects anyways seem negligible. As the mesh size also influences diffusivity, the cross-linker amount is found to determine the magnitude of the investigated effect.

As described previously, the free volume of the thin films accessible to water vapor has been investigated. The magnitude of the initial refractive index increase while introducing water vapor into the nitrogen filled system can display differences in the available free volume (see Figure 6). The refractive index difference is found constant for both cross-linker series and shows just one smaller value for the lowest film thickness of the

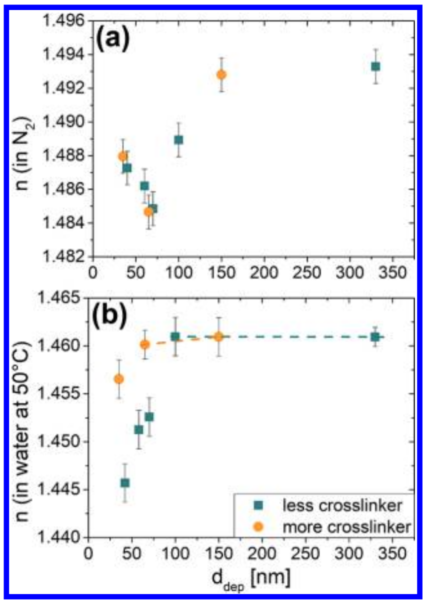


Figure 5. Refractive index n (measured at 633 nm) (a) in nitrogen environment at 25 °C and (b) in water at 50 °C after heating (collapsed state) of the polymer layers plotted as a function of deposited film thickness (d_{dep}) as measured by spectroscopic ellipsometry (dotted lines are for guidance of the eye).

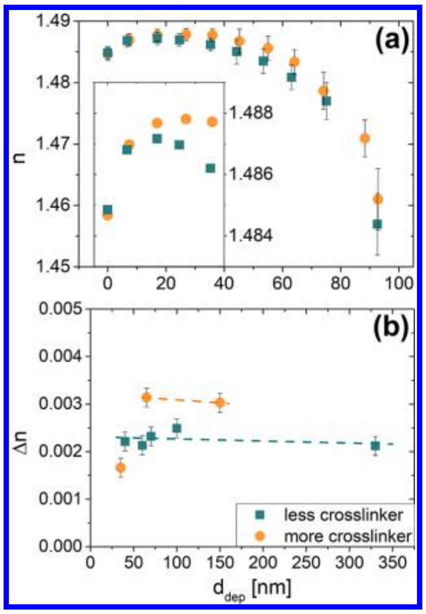


Figure 6. (a) Refractive index n (at 633 nm) as measured via SE during relative humidity exposure of two differently cross-linked 70 nm-thick p(NIPAAm-*co*-DEGDVE) samples (the inset shows a zoom of the region below 40% relative humidity, where the increase in refractive index Δn was evaluated). (b) Refractive index difference Δn as a measure of the free volume of the thin films prone to uptake of water vapor plotted as a function of deposited film thickness d_{dep} (dotted lines are for guidance of the eye).

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more cross-linked samples (see Figure 6a). This hints no influence of the free volume accessible via this water uptake on the thickness dependence of the LCST. However, the refractive index difference is lower for the less cross-linked series. As mentioned previously, the less cross-linked films swell more than the more cross-linked ones. As swelling also occurs in humidity and causes the refractive index to decrease, it leads to a lower refractive index difference for the less cross-linked samples (see Figure 6b). Hence, the free volume is only partially probed. The water molecules just adsorb up to a point where swelling is more prominently observed in refractive index behavior. Therefore, the shape and position of the LCST, swelling in humidity, and density are possibly influencing this measurement as well as just the adsorption of water molecules into the free volume of the investigated polymeric systems. However, the investigated films swell already by changing the environment from 0 to 10% RH (see the Supporting Information), which is promising for utilization in sensing applications.

To deepen the understanding of the results of the refractive index measurements in a nitrogen environment (see Figure 5a), XRR measurements have been used to investigate the density of the thin films. The position of the critical angle of total reflection is proportional to the electron density of the investigated layers.[19] By assuming the nominal percentages of cross-linking and knowing the molecular weight and number of electrons of the respective monomers, an estimation of the mass density of the investigated thin films could be derived. For that, the average number of electrons of an individual polymeric structure can be assumed to be constant for films of the same composition in one series of similar cross-linking. Therefore, the mass density evaluated from the XRR measurements has been plotted as a function of deposited film thickness for different amounts of cross-linking (see Figure 7). The mass density values are found to lie in a range of 1.1–1.3 g/cm^3, which is in agreement with literature values. The mass density of emulsion polymerized pNIPAAm microgels cross-linked by 2.5 mol% *N*,*N*′-methylenbis(acrylamide) (BIS) has been reported to be around 1.15 g/cm^3.[24] The differences in cross-linking (amount and chemical nature) and different polymerization techniques account for the differences in density reported in the present work. In the thickness study, the density decreases in the low film thickness regime of up to ~70 nm for both cross-linker series. At higher film thickness, the density increases again, with values surpassing the ones at low film thickness. Overall, the mass density of the more cross-linked thin films has been evaluated to be higher than the one of the less cross-linked samples. Therefore, XRR results are found to be in agreement with the refractive index as measured with SE in a nitrogen environment (see Figure 5a) and mimic the trend of the LCST values as a function of deposited film thickness for both cross-linker series with inverse proportionality. Not knowing the exact compositions, the exact polymer molecular weight and, therefore, also the exact number of electrons of the polymeric structures results in large error bars of the mass density estimates. However, the measured critical angles of total reflection (see the Supporting Information) infer a correlation between the density of the polymeric matrix and the position of the LCST of the respective p(NIPAAm-*co*-DEGDVE) thin film samples.

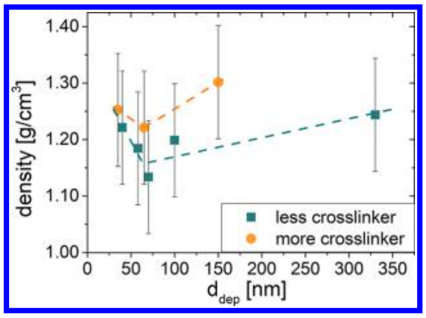

Figure 7. Mass density as calculated from the critical angle of total reflection evaluated from XRR measurements as a function of deposited film thickness (d_{dep}) for differently cross-linked sample series (dotted lines are for guidance of the eye).

As aforementioned, by choosing a slow heating rate (0.5 °C/min), the chance of kinetic effects interfering with the evaluation of the LCST from the SE measurements in water has been minimized. Long-term kinetic effects cannot be ruled out, as it has been reported to take polyelectrolyte thin films several days to reach a constant film thickness during swelling in relative humidity.[25] In addition, a difference in density among thin films of different thicknesses is generally caused by a variation of the deposition conditions. However, similar deposition rates, in the range 1.6–2.0 nm/min, were measuredfor all of the investigated samples in the case studies, excluding fluctuations of this parameter having an effect on the molecular weight of the resulting thin films.[20] In the literature, Bonnet et al. reported two growth regimes in iCVD polymerization of p(neo-pentyl methacrylate) thin films, stating that the initial stages of a deposition exhibit a lower deposition rate and therefore yield lower molecular weight thin films.[26] In the present study, no significant variation of the deposition rate has been observed via *in situ* laser interferometry upon deposition. Overall, the deposition rate has not been noted to change more than 10% over time during a single deposition process. Bonnet et al. also did not report on changes in the density of the investigated thin films;[26] although the changes in density are delicate in the present work, they lead to consistent and significant changes in swelling behavior. A possible explanation would be local depletion of monomer at the substrate level during one deposition with time, as higher cross-linking would lower the LCST, as described previously. This would lead to a gradient of cross-linking, with high film thickness samples exhibiting more cross-linking and therefore lower LCST values. However, the maximum swelling was comparable for the similarly cross-linked samples within a thickness series (120 and 60% swelling for the less and more cross-linked films at 20 °C, respectively), pointing out that a gradient in cross-linking in the layer can be excluded, as it would possibly also lead to an altered maximum swelling value. In the film thickness range up to ~70 nm, the opposite LCST behavior compared to the region above 70 nm has been observed. In particular, the LCST was found to decrease toward lower film thickness, but still, the maximum swelling of the corresponding films compared well to the ones of the films with higher LCSTs of similar cross-linking. In contrast to the photo-cross-linked thin films reported on by Harmon et al.,[13] the iCVD thin films grow steadily from the substrate with cross-linking happening during film growth. Hypothetically, the copolymerization of the two chemical species used in the present work, NIPAAm and DEGDVE, yields local differences in composition and morphology of the thin films, resulting in differences of the average mass density of the resulting thin

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films. These differences then lead to a variation of the swelling behavior and therefore of the LCST transition.

■ CONCLUSIONS

In this work, pNIPAAm-based thin films have been successfully prepared with different degrees of cross-linking and film thickness by iCVD. The understanding of the shape and position of their LCST transition has been deepened, as effects of both cross-linking and film thickness have been investigated. Increasing the DEGDVE cross-linker amount leads to a lower maximum swelling degree and a lower LCST. (Mass) density (as evaluated from SE and XRR) mimics the trends of the LCST as a function of cross-linking and deposited film thickness. Hence, an increase in the density of the polymeric matrix leads to a decrease in the transition temperature. The density in the dry state can be increased by adding more cross-linker. Both investigated thickness series exhibit a maximum density at a film thickness of about 70 nm, leading to a minimum in LCST for the respective similarly cross-linked thickness series. As deposition conditions within the thickness series have been carefully set constant, either local fluctuations in the reaction chamber or differences in the copolymerization procedure of NIPAAm and DEGDVE over time during one deposition process have been deemed responsible for the differences in density as a function of film thickness. When the polymer is cross-linked in the dry state, thickness-dependent compression leads to a lower LCST at higher film thickness.[13] The present work provides a further understanding of the proposed hypothesis and adds to it the correlation to the mass density of the polymeric thin films. The role of gradients in water diffusivity due to the substrate−polymer interface altering the hydrophobicity within the investigated systems as a function of film thickness needs to be further addressed. However, these detailed insights should raise awareness about the influence of growth conditions as well as behavior on a plethora of material's properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.8b02120.

> Swelling in humidity of p(NIPAAm-*co*-DEGDVE) thin films of different cross-linker amount, several heating ramps in water of different p(NIPAAm-*co*-DEGDVE) samples, and critical angle of total reflection of p(NIPAAm-*co*-DEGDVE) thin film samples as read out from X-ray reflectivity measurements (PDF)

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Notes

The authors declare no competing financial interest.

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